

Third Edition

ORGANIC CHEMISTRY

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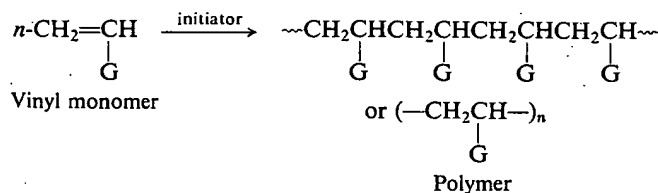
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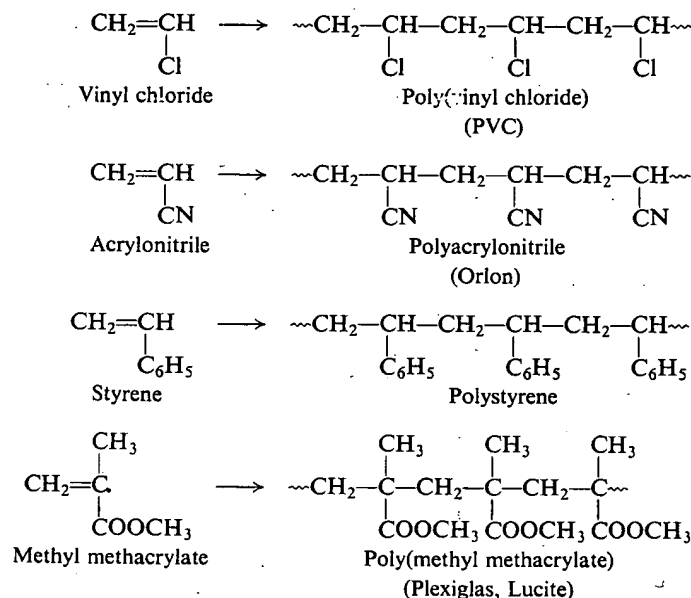
Problem 32.2 Answer the questions of Problem 32.1 for each of the following kinds of natural macromolecules: (a) a protein, p. 1151; (b) a nucleic acid, p. 1178; (c) starch (amylose), p. 1121; (d) cellulose, p. 1126.

32.3 Free-radical vinyl polymerization

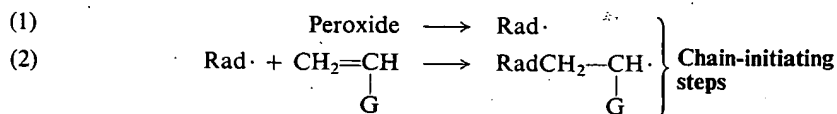
In Sec. 6.19 we discussed briefly the polymerization of ethylene and substituted ethylenes under conditions where free radicals are generated—typically in the presence of small amounts of an initiator, such as a peroxide. Reaction

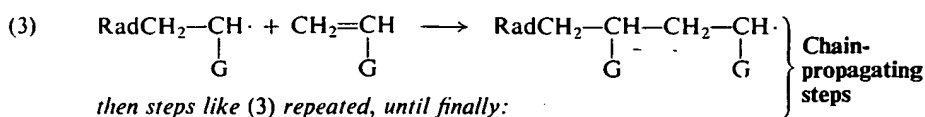


occurs at the doubly-bonded carbons—the vinyl groups—and is called *vinyl polymerization*. A wide variety of unsaturated monomers may be used, to yield polymers with different *pendant groups* (G) attached to the polymer backbone. For example:

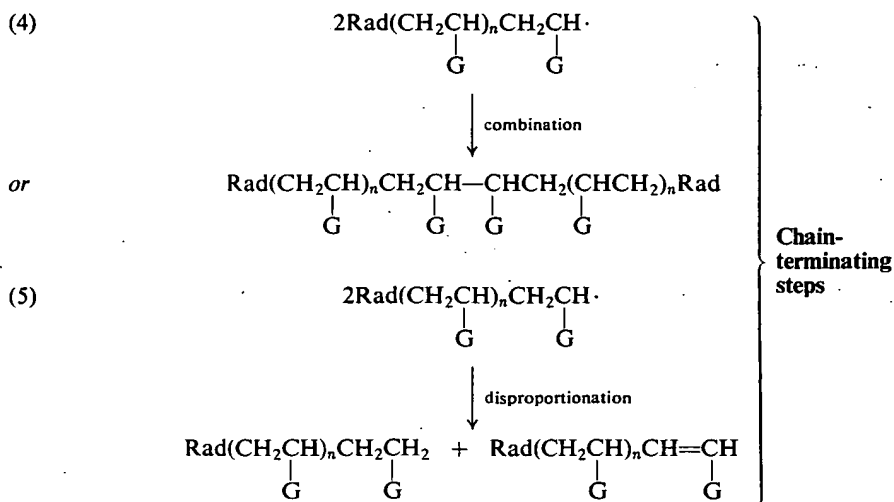


Polymerization involves addition of free radicals to the double bond of the monomer: addition, first, of the free radical generated from the initiator, and then of the growing polymer molecule. This is, of course, an example of chain-reaction polymerization.





then steps like (3) repeated, until finally:



In each step the consumption of a free radical is accompanied by the formation of a new, bigger free radical. Eventually, the reaction chain is terminated by steps that consume but do not form free radicals: *combination* or *disproportionation* of two free radicals.

Problem 32.3: Free-radical polymerization of 1,4-bisazidene gives molecules that contain both the following units:

$-\text{CH}_2\text{CH}(\text{CH}_2\text{CH})_n\text{CH}_2\text{CH}-$ and $-\text{CH}_2\text{CH}(\text{CH}_2\text{CH})_m\text{CH}=\text{CH}-$

the exact proportions depending on the temperature. Account in detail for the formation of the two different units.

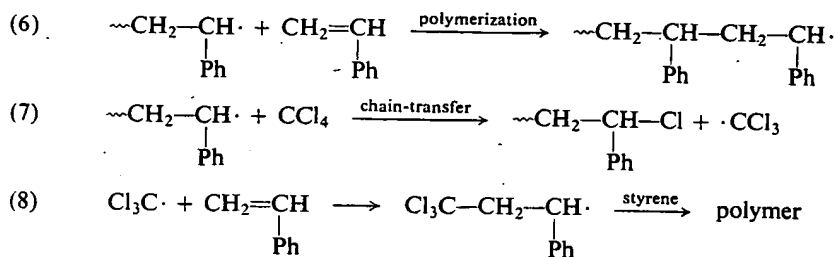
Problem 32.4: Polystyrene formed with isotopically labeled AIBN as initiator was found to contain 1/2 initiator fragments per molecule. What termination reaction is indicated by this finding?

$(\text{CH}_3)_2\text{C}(\text{CN})-\text{N}=\text{N}-\text{C}(\text{CN})_2 \longrightarrow 2(\text{CH}_3)_2\dot{\text{C}}(\text{CN})$

Azobisisobutyronitrile (AIBN)

Added compounds can modify the polymerization process drastically. For example, in the presence of carbon tetrachloride, styrene undergoes polymerization at the same rate as in its absence, but the polystyrene obtained has a lower average molecular weight; furthermore, it contains small amounts of chlorine.

This is an example of **chain-transfer**, the termination of one polymerization chain (7) with the simultaneous initiation of another (8).



Ordinarily a growing polystyrene radical adds (6) to styrene monomer to continue the reaction chain. Every so often, however, it abstracts an atom from the chain-transfer agent (7) to end the original polymerization chain and generate a new particle ($\text{CCl}_3\cdot$ in this case) that initiates a new polymerization chain (8). Since one reaction chain is replaced by another, the rate of polymerization is unaffected. Since the average number of chain-propagating steps in each reaction chain is reduced, the average molecular weight of the polymer is lowered. A transfer agent thus competes with the monomer for the growing radicals. The ratio of rate constants for (7) and (6), $k_{\text{transfer}}/k_{\text{polymerization}}$, is called the *transfer constant*; it is a measure of how effective the transfer agent is at lowering the molecular weight of the polymer.

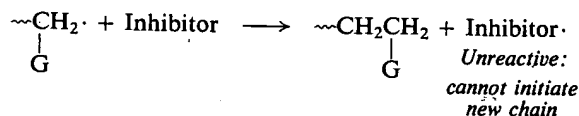
Problem 32.5. For polymerization of styrene at 60°C the following chain-transfer constants have been measured. Account for the relative differences of the members of each sequence.

(a) benzene 0.018, 2,2-burylbenzene 0.04, toluene 0.125, ethylbenzene 0.67, isopropylbenzene 0.86

(b) 7-heptane 0.42, 2-heptene 2.7

(c) CCl_4 90, CBr_4 3600

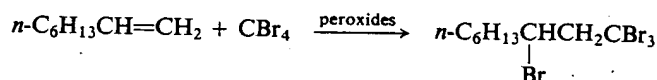
An added compound may react with the growing free radical to generate a new free radical that is not reactive enough to add to monomer; a reaction chain is terminated but no new one is begun. Such a compound is, of course, an **inhibitor** (Sec. 2.14). Many amines, phenols, and quinones act as inhibitors. Although their exact mode of action is not understood, it seems clear that they are converted into free radicals that do not add to monomer; instead, they may combine or disproportionate, or combine with another growing radical to halt a second reaction chain.



Since even traces of certain impurities, acting as chain-transfer agents or inhibitors, can interfere with the polymerization process, the monomers used are among the purest organic chemicals produced.

In an extreme case—if the alkene is of low reactivity and the transfer agent of high reactivity—chain transfer is so effective that there is *no* polymerization. Then

we observe simply addition of the "transfer agent" to the double bond, a reaction we encountered in Sec. 6.18. For example:

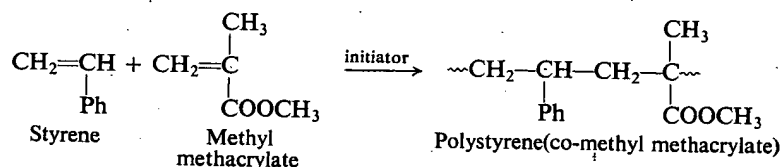


Problem 32.6 (a) Chain transfer can cause *branching* of a polymer molecule. Show how this could happen. What is the chain transfer agent? (b) Rather short branches (4 or 5 carbons) are attributed to "back-biting." What do you think is meant by this term? Show the chemical reactions probably involved.

32.4 Copolymerization

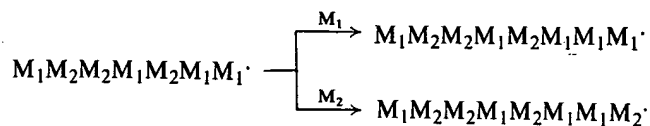
So far, we have discussed only polymerization of a single monomeric compound to form a *homopolymer*, a polymer made up—except, of course, at the two ends of the long molecule—of identical units.

Now, if a mixture of two (or more) monomers is allowed to undergo polymerization, there is obtained a **copolymer**: a polymer that contains two (or more) kinds of monomeric units in the same molecule. For example:



Through copolymerization there can be made materials with different properties than those of either homopolymer, and thus another dimension is added to the technology. Consider, for example, styrene. Polymerized alone, it gives a good electric insulator that is molded into parts for radios, television sets, and automobiles. Copolymerization with butadiene (30%) adds toughness; with acrylonitrile (20–30%) increases resistance to impact and to hydrocarbons; with maleic anhydride yields a material that, on hydrolysis, is water-soluble, and is used as a dispersant and sizing agent. The copolymer in which butadiene predominates (75% butadiene, 25% styrene) is an elastomer, and since World War II has been the principal rubber substitute manufactured in the United States.

Let us look more closely at the copolymerization process. Consider free radical vinyl polymerization of two monomers, M_1 and M_2 . In each step the growing free



radical can react with either monomer to continue the reaction chain. What are the factors that determine *which* monomer it preferentially reacts with?

First, of course, there are the relative *concentrations* of the two monomers; the higher the concentration of a particular monomer, the greater its chance of

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